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# Chemical-Specific Parameters for Toxicity Characteristic Contaminants

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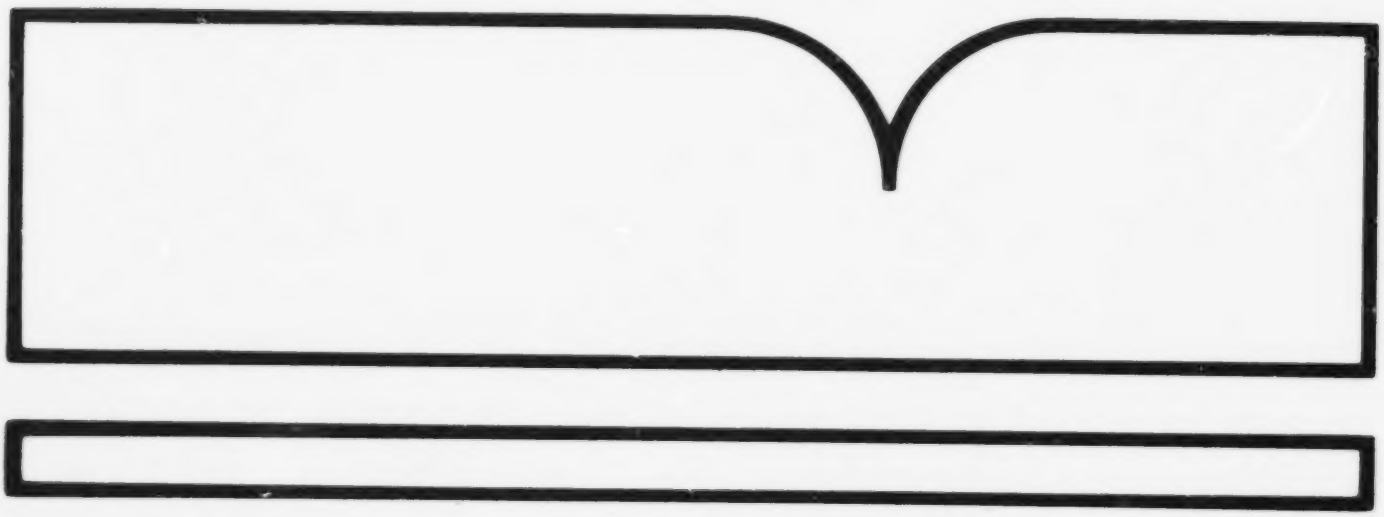

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# CHEMICAL-SPECIFIC PARAMETERS FOR TOXICITY CHARACTERISTIC CONTAMINANTS

by

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Acid, base, and neutral hydrolysis rate constants and partition coefficients are given for 44 toxicity characteristic contaminants. Both calculated and laboratory-determined octanol/water partition coefficient ($K_{OW}$) and organic-carbon-normalized partition coefficient ($K_{OC}$) values are included. Log $K_{OC}$ values were calculated at pH 7 for ten ionizable acids and one ionizable base.

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## FOREWORD

As environmental controls become more expensive and the penalties of judgment errors become more severe, environmental management requires more precise tools based on greater knowledge of relevant phenomena. As part of this Laboratory's research on the occurrence, movement, transformation, impact, and control of chemical contaminants, the Measurements Branch determines the occurrence of unexpected organic pollutants in the aquatic environment and develops and applies techniques to measure physical, chemical, and microbial transformation and equilibrium constants for use in assessment models and for development of property-reactivity correlations.

The Resource Conservation and Recovery Act requires the U.S. Environmental Protection Agency to develop and promulgate criteria for identifying and listing hazardous wastes. Among the listed chemicals are compounds of concern because of their potential toxicity should they leach from a disposal site. This report provides hydrolysis rate constants and sorption equilibrium constants for 44 chemicals that can be applied in simulation models or other techniques for assessing potential risk from environmental exposure.

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## ABSTRACT

Acid, base, and neutral hydrolysis rate constants and partition coefficients are given for 44 toxicity characteristic contaminants. Both calculated and laboratory-determined octanol/water partition coefficient ($K_{ow}$) and organic-carbon-normalized partition coefficient ($K_{oc}$) values are included. Log $K_{oc}$ values were calculated at pH 7 for ten ionizable acids and one ionizable base.

## ACKNOWLEDGMENTS

The contribution of Dr. Peter M. Jeffers in characterizing the hydrolysis mechanisms and hydrolysis rate constants for the various halogenated methanes, ethanes and aromatics is gratefully acknowledged. The typing of the manuscript and editorial suggestions by Ms. Mimi Houston during preparation of the report are also gratefully acknowledged. The authors also thank Drs. Leo Azarraga and Timothy Collette for their timely review of this manuscript.

# INTRODUCTION

Assessment of potential risk posed to humans by man-made chemicals in the environment requires the prediction of environmental concentrations of those chemicals under various environmental reaction conditions. Whether mathematical models or other assessment techniques are employed, knowledge of equilibrium and kinetic constants (fate constants) is required to predict the transport and transformation of these chemicals.

Under section 301 of the Resource Conservation and Recovery Act (RCRA), EPA's Office of Solid Waste (OSW) has identified wastes that may pose a substantial hazard to human health and the environment. RCRA requires that EPA develop and promulgate criteria for identifying and listing hazardous wastes, taking into account, among other factors, persistence and degradability in the environment.

In 1986, OSW proposed additions to the list of chemicals regulated under the Toxicity Characteristic section of RCRA. A land disposal decision model developed at the Environmental Research Laboratory in Athens, Georgia (ERL-Athens) was applied to determine maximum permissible leachate concentrations resulting from the Toxicity Characteristic Leachate Procedure for the additional chemicals. This report includes hydrolysis rate constants and sorption equilibrium constants for 44 "toxicity characteristic" contaminants.

## SECTION 1

## Hydrolysis of Toxicity Characteristic Contaminants

### 1.1 Background

In general, hydrolysis is a bond-making, bond-breaking process in which a molecule, RX, reacts with water forming a new R-O bond and cleaving a R-X bond in the original molecule. One possible pathway is by a direct displacement of $X^-$ with $HO^-$ as shown in Equation 1 (1).

$$RX + HO^- \xrightarrow{H_2O} ROH + X^- \quad (1)$$

The detailed mechanisms of hydrolytic processes are well defined and have been shown to involve the formation of intermediates such as protonated species, anions and carbonium ions, as well as combinations of these intermediates.

In general, hydrolysis of organic chemicals in water under pH-buffered conditions is first-order in the concentration of the organic species ([RX]), where the rate of hydrolysis ($d[RX]/dt$) is proportional to the concentration of pollutant RX:

$$d[RX]/dt = -k_{obs}[RX] \quad (2)$$

where $k_{obs}$ is the observed pseudo-first-order disappearance rate constant. The first-order dependence of the disappearance rate on [RX] is important, because it means that the half-life ($t_{1/2}$) of the reaction described by Equation 2 is independent of [RX]. Thus, the results obtained at a high RX concentration can be extrapolated to lower RX concentrations if other reaction conditions are held constant. The half-life of the reacting compound is given in Equation 3:

$$t_{1/2} = \ln(2)/k_{obs} = 0.693/k_{obs} \quad (3)$$

where $k_{obs}$ can include contributions from acid catalyzed or base mediated hydrolysis, nucleophilic attack by water, or catalysis by buffers in the reaction medium. Hydrolysis half-lives conveniently put in perspective the susceptibility of pesticides to hydrolysis at a given pH (2).

For abiotic hydrolysis, the general expression for $k_{obs}$ is given by:

$$k_{obs} = k_a[H^+] + k_b[OH^-] + k_n + \sum_i k_{HA}[HA] + k_A[A^-] \quad (4)$$

where $k_a$ and $k_b$ are the specific acid and base second-order rate constants, respectively; $k_n$ is the neutral hydrolysis rate constant; and $k_{HA}$ and $k_A$ are the general acid and base catalyzed hydrolysis rate constants, respectively. In Equation 4, $[H^+]$ and $[OH^-]$ are the hydrogen and hydroxyl ion concentrations, respectively, and [HA] and $[A^-]$ are the concentrations of the ith pair of general acids and bases in the reaction mixture.

## 1.2 Hydrolysis Rate Constants

In Tables 1 through 5, the 44 toxicity characteristic contaminants are combined by functional group. Contaminants without partners were combined to form the list of miscellaneous chemicals in Table 5. For those compounds identified as having no hydrolyzable functional groups (NHFG), hydrolysis will not occur by abiotic reaction pathways in the pH range of 5 to 9 at 25°C. The types of compounds included in this field are aliphatic hydrocarbons, aromatic hydrocarbons, phenols, and alcohols.

A second classification consisted of chemicals that have non-labile functional groups (NLFG). Although a molecule with a non-labile functional group contains one or more heteroatoms, they are so unreactive that they will not hydrolyze to any reasonable extent. Over the pH range of 5 to 9 at 25°C, half-lives will be greater than 50 years if they react at all.

In Tables 1 through 5, $k_a$, $k_b$, and $k_n$ values are reported for the particular chemical at 25°C. A half-life at 25°C can be calculated by using Equation 4 to calculate $k_{obs}$ followed by Equation 3 to calculate the time at 50% hydrolysis. Concentration and time units used are molar (M) and year (y), respectively.

### 1.2.1 Phenols

Hydrolysis will not have to be considered for these phenols. They contain no hydrolyzable functional groups (NHFG) (3).

TABLE 1. PHENOLS, 25°C

| CHEMICAL NAME | CAS NO. | $k_a$ ($M^{-1} y^{-1}$) | $k_n$ $y^{-1}$ | $k_b$ ($M^{-1} y^{-1}$) | Comment | Reference |
|---|---|---|---|---|---|---|
| M-CRESOL | 108-39-4 | 0 | 0 | 0 | NHFG | 3 |
| O-CRESOL | 95-48-7 | 0 | 0 | 0 | NHFG | 3 |
| P-CRESOL | 106-44-5 | 0 | 0 | 0 | NHFG | 3 |
| PHENOL | 108-95-2 | 0 | 0 | 0 | NHFG | 3 |

### 1.2.2 Aromatic Hydrocarbons

Hydrolysis will not have to be considered for the hydrocarbons. Hydrocarbons contain only carbon-hydrogen bonds and thus contain no hydrolyzable functional groups (NHFG) (3).

Table 2. HYDROCARBONS, 25°C

| CHEMICAL NAME | CAS NO. | $k_a$ ($M^{-1} y^{-1}$) | $k_n$ $y^{-1}$ | $k_b$ ($M^{-1} y^{-1}$) | Comment | Reference |
|---|---|---|---|---|---|---|
| BENZENE | 71-43-2 | 0 | 0 | 0 | NHFG | 3 |
| TOLUENE | 108-88-3 | 0 | 0 | 0 | NHFG | 3 |

### 1.2.3 Halogenated Aromatics

Because of inherent differences in the hydrolysis mechanisms of halogenated aliphatic hydrocarbons and halogenated aromatic hydrocarbons, their hydrolytic reactivity is addressed separately.

No reliable hydrolysis rate constants for halogenated aromatics are available in the literature and attempts to determine degradation rate constants for selected halogenated aromatics under extremely harsh reaction conditions have resulted in no detectable reaction of any compound. The most facile reaction would be alkaline hydrolysis because of high nucleophilicity of the hydroxide ion in water. The following reaction conditions demonstrated the hydrolytic stability of this class of compounds; in each experiment, there was no detectable change in concentration of the compounds within experimental error.

| | | | |
|---|---|---|---|
| p-chlorotoluene | 0.1 M NaOH | 170°C | 8 days |
| p-chlorobenzoic acid | 0.5 M NaOH | 174°C | 22 hrs. |
| p-bromobenzoic acid | 0.5 M NaOH | 174°C | 22 hrs. |
| p-chlorobenzoic acid | 0.5 M NaOH | 174°C | 21 days |
| p-bromobenzoic acid | 0.5 M NaOH | 174°C | 21 days |
| 2,6-dichlorobenzoic acid | 0.4 M NaOH | 170°C | 44 hrs. |
| 2,5-dichlorobenzoic acid | 0.4 M NaOH | 170°C | 44 hrs. |
| 3,5-dichlorobenzoic acid | 0.4 M NaOH | 170°C | 44 hrs. |
| 3,5-dichlorobenzoic acid | 0.4 M NaOH | 170°C | 44 hrs. |
| 3,4-dichlorobenzoic acid | 0.4 M NaOH | 170°C | 44 hrs. |

Assuming a 10% error in measuring the concentration of the compound, i.e., 10% did actually hydrolyze, we can calculate a maximum rate constant. Using average activation parameters for the halogenated aromatic hydrocarbons, we can extrapolate this maximum calculated rate constant to the standard temperature of 25°C. Thus at 25°C, $k_b = 1.4 \times 10^{-9}$ $M^{-1}$ $min^{-1}$ and $k_n = 1.4 \times 10^{-10}$ $min^{-1}$, which gives an estimated minimum half-life of 10,000 years at 25°C and pH 7 (4a).

Thus, although the carbon-chlorine bond can potentially undergo hydrolysis, it is not reactive when the carbon atom is an aromatic ($sp^2$) carbon. Consequently, all the compounds in Table 3 are labelled NLFG. Silvex was included in Table 3 because of its chlorinated aromatic moiety.

Table 3. HALOGENATED AROMATICS, 25°C

| CHEMICAL NAME | CAS NO. | $k_a$ ($M^{-1} y^{-1}$) | $k_n$ $y^{-1}$ | $k_b$ ($M^{-1} y^{-1}$) | Comment | Reference |
|---|---|---|---|---|---|---|
| CHLOROBENZENE | 108-90-7 | 0 | 0 | 0 | NLFG | 3,4a |
| 1,4-DICHLOROBENZENE | 106-46-7 | 0 | 0 | 0 | NLFG | 3,4a |
| 1,2-DICHLOROBENZENE | 95-50-1 | 0 | 0 | 0 | NLFG | 3,4a |
| HEXACHLOROBENZENE | 118-74-1 | 0 | 0 | 0 | NLFG | 3,4a |
| PENTACHLOROPHENOL | 87-86-5 | 0 | 0 | 0 | NLFG | 3,4a |
| SILVEX (2,4,5-TP) | 93-72-1 | 0 | 0 | 0 | NLFG | 3,4a |
| 2,3,4,6-TETRACHLOROPHENOL | 58-90-2 | 0 | 0 | 0 | NLFG | 3,4a |
| 2,4,5-TRICHLOROPHENOL | 95-95-4 | 0 | 0 | 0 | NLFG | 3,4a |
| 2,4,6-TRICHLOROPHENOL | 88-06-2 | 0 | 0 | 0 | NLFG | 3,4a |

### 1.2.4 Halogenated Aliphatics

Bis(2-chloroethyl) ether undergoes a very fast neutral hydrolysis as a result of neighboring group participation by the oxygen atom. Rate constants have been measured for the stepwise hydrolysis of both chlorines. This ether was included in Table 4 because the reactive center is the C-Cl bond.

Carbon tetrachloride undergoes hydrolysis by a neutral process that proceeds by nucleophilic substitution by water at the carbon atom. No alkaline hydrolysis contribution has been detected in 0.1 M NaOH at 140°C for 7 days (4a).

Chlordane undergoes alkaline hydrolysis and the experimental rate constant is consistent with the value estimated using a structure activity relationship (SAR) developed for the haloaliphatics (4b).

Chloroform undergoes neutral and alkaline hydrolysis. Both of these rate constants have been determined experimentally.

1,2-Dichloroethane undergoes hydrolysis by neutral and alkaline pathways. Both rate constants have been determined experimentally. The alkaline pathway is consistent with the second-order alkaline hydrolysis mechanism and the neutral hydrolysis is consistent with a nucleophilic substitution mechanism.

1,1-Dichloroethylene undergoes alkaline hydrolysis and the experimental value has been determined (4a). This is consistent with the SAR for alkaline hydrolysis of haloaliphatics (4b). Because there are no activated hydrogen atoms, general base catalysis is not an important reaction under neutral conditions. Also because the chlorines are attached to $sp^2$ carbons, nucleophilic substitution will be too slow to be detected under the reaction conditions described above.

Heptachlor contains an allylic chlorine, which is the most reactive functional group. This compound undergoes neutral hydrolysis. The rate constant has been determined experimentally.

Hexachloro-1,3-butadiene has no hydrogen atoms, thus, hydroxide ion mediated elimination is not a possible reaction pathway. Because the chlorines are all attached to $sp^2$ carbon atoms, they also will not be facile to neutral hydrolysis (NLFG).

Hexachloroethane has no hydrogen atoms and will not undergo alkaline elimination. Because of the steric hinderance posed by the three chlorines at each carbon atom, the compound will not undergo hydrolysis by nucleophilic substitution by hydroxide ion or water. Furthermore, because of carbonium ion destabilization by the chlorines, this compound will not undergo facile hydrolysis by an $S_N1$ mechanism (NLFG).

Lindane undergoes both alkaline and neutral hydrolysis and these rate constants have been determined experimentally.

Methoxychlor's alkaline and neutral hydrolysis rate constants have been experimentally determined. Calculation of the alkaline hydrolysis rate constant using the SAR (4b) gave a value of $1.2 \times 10^4$ $M^{-1}$ $y^{-1}$. It is not possible to accurately calculate the neutral hydrolysis rate constant because of the neighboring group enhancement of hydrolysis for this pathway. The calculated value would be much larger than the measured value.

The neutral hydrolysis rate constant has been experimentally determined for methylene chloride. The calculated rate constant using the SAR (4b) for neutral hydrolysis is $1.4 \times 10^{-4}$ $y^{-1}$ which is in reasonable agreement with the measured value. The calculated alkaline hydrolysis rate constant is $3.4 \times 10^3$ $M^{-1}$ $y^{-1}$.

The alkaline and neutral hydrolysis rate constants have been measured for 1.1.1.2-tetrachloroethane. Based on the SAR, these values are consistent with alkaline hydrolysis at high pH's and general base catalysis at lower pH's.

Both neutral and alkaline hydrolysis rate constants have been measured for 1.1.2.2-tetrachloroethane. The numbers are consistent with the SAR's (4b).

Hydrolysis of tetrachloroethylene could not be detected in 0.1 M NaOH at 140°C for 7 days (4). This is consistent with the fact that there are no hydrogen atoms on the molecule and the chlorines are attached to $sp^2$ carbon atoms.

Toxaphene is a complex mixture of chlorinated terpenes and an over-all disappearance rate constant has been measured for the mixture. Components of the mixture undergo both neutral and alkaline hydrolysis.

1.1.1-Trichloroethane undergoes neutral hydrolysis and the rate constant has been measured.

Both the neutral and alkaline hydrolysis rate constants have been measured for 1.1.2-trichloroethane. These rate constants are consistent with the SAR's (4b) for second-order alkaline elimination and general base elimination reaction mechanisms.

The alkaline hydrolysis rate constant has been measured for trichloroethylene. There was no detectable change in trichloroethylene concentration at pH 3 at 140°C after 7 days and thus no neutral hydrolysis rate constant could be calculated. The experiment was performed at pH 3 to minimize any contribution of hydroxide ion.

Maximum rate constants have been estimated for vinyl chloride based on experimental observations. The estimated rate constant based on the alkaline SAR (4b) is 0.08 $M^{-1}$ $y^{-1}$, which is consistent with the experimental values in Table 4. Based on the neutral hydrolysis SAR (4b), there should not be a neutral hydrolysis contribution.

Table 4. HALOGENATED ALIPHATICS, 25°C

| CHEMICAL NAME | CAS NO. | $k_a$ ($M^{-1}\,y^{-1}$) | $k_n$ $y^{-1}$ | $k_b$ ($M^{-1}\,y^{-1}$) | Comment | Reference |
|---|---|---|---|---|---|---|
| BIS(2-CHLOROETHYL) ETHER | 111-44-4 | 0 | 0.23 | 0 | MEASURED | 5 |
| CARBON TETRACHLORIDE | 56-23-5 | 0 | 0.017 | 0 | MEASURED | 6 |
| CHLORDANE, TECHNICAL (CIS) | 57-74-9 | 0 | 0 | 37.7 | MEASURED | 7 |
| CHLOROFORM | 67-66-3 | 0 | 1.00E-4 | 2.74E3 | MEASURED | 6 |
| 1,2-DICHLOROETHANE | 107-06-2 | 0 | 9.61E-3 | 54.7 | MEASURED | 6 |
| 1,1-DICHLOROETHYLENE (VINYLIDENE CHLORIDE) | 75-35-4 | 0 | 0 | 5.7E-2 | MEASURED | 6 |
| HEPTACHLOR | 76-44-8 | 0 | 56 | 0 | MEASURED | 8 |
| HEXACHLORO-1,3-BUTADIENE | 87-68-3 | 0 | 0 | 0 | NLFG | 4b |
| HEXACHLOROETHANE | 67-72-1 | 0 | 0 | 0 | NLFG | 6 |
| LINDANE (HEXACHLOROCYCLOHEXANE) | 58-89-9 | 0 | 1.05 | 1.74E6 | MEASURED | 7 |
| METHOXYCHLOR | 72-43-5 | 0 | 0.69 | 1.2E4 | MEASURED | 9 |
| METHYLENE CHLORIDE | 75-09-2 | 0 | 1.01E-3 | 0 | MEASURED | 10 |
| 1,1,1,2-TETRACHLOROETHANE | 630-20-6 | 0 | 1.37E-2 | 1.13E4 | MEASURED | 6 |
| 1,1,2,2-TETRACHLOROETHANE | 79-34-5 | 0 | 5.10E-3 | 1.56E7 | MEASURED | 6 |
| TETRACHLOROETHYLENE (PERCHLOROETHYLENE) | 127-18-4 | 0 | 0 | 7.2E-3 | MEASURED | 6 |
| TOXAPHENE | 8001-35-2 | 0 | 7.0E-2 | 2.8E4 | MEASURED | 7 |
| 1,1,1-TRICHLOROETHANE | 71-55-6 | 0 | 0.65 | 0 | MEASURED | 6 |
| 1,1,2-TRICHLOROETHANE | 79-00-5 | 0 | 2.73E-5 | 4.95E4 | MEASURED | 6 |
| TRICHLOROETHYLENE | 79-01-6 | 0 | 0 | 5.62 | MEASURED | 6 |
| VINYL CHLORIDE | 75-01-4 | 0 | <7.0E-2 | <3.5 | MEASURED | 11 |

### 1.2.5 Miscellaneous Chemicals

The remaining nine chemicals that did not fit into the chemical groups listed above were placed into the miscellaneous group. Hydrolysis rate constants have been measured for two of the chemicals in this group. At pH 7, the hydrolytic half-lives for acrylonitrile and carbon disulfide will be 1,222 y and 220 y, respectively. The other chemicals contain either non-hydrolyzable or non-labile functional groups, thus, their hydrolysis will not have to be considered.

Table 5. MISCELLANEOUS CHEMICALS, 25°C

| CHEMICAL NAME | CAS NO. | $k_a$ ($M^{-1} y^{-1}$) | $k_n$ $y^{-1}$ | $k_b$ ($M^{-1} y^{-1}$) | Comment | Reference |
|---|---|---|---|---|---|---|
| ACRYLONITRILE | 107-13-1 | 3.7E2 | 0 | 5.3E3 | MEASURED | 12a |
| CARBON DISULFIDE | 75-15-0 | 0 | 0 | 3.15E4 | MEASURED | 13 |
| 2,4-D | 94-75-7 | 0 | 0 | 0 | NLFG | 3 |
| ENDRIN | 72-20-8 | 0 | (5.5±0.5)E-2 | 0 | a | 12b |
| ISOBUTANOL (ISOBUTYL ALCOHOL) | 78-83-1 | 0 | 0 | 0 | NHFG | 3 |
| METHYL ETHYL KETONE | 78-93-3 | 0 | 0 | 0 | NHFG | 3 |
| NITROBENZENE | 98-95-3 | 0 | 0 | 0 | NLFG | 3 |
| PYRIDINE | 110-86-1 | 0 | 0 | 0 | NHFG | 3 |
| 2,4-DINITROTOLUENE | 121-14-2 | 0 | 0 | 0 | NLFG | 3 |

a. A protocol developed for measuring hydrolysis rate constants (12b) was used to determine the hydrolysis rate constant for endrin.

## SECTION 2

## Partition Coefficients of Toxicity Characteristic Contaminants

### 2.1 Neutral Organic Compounds

Partitioning between water and natural soils, sediments and aquifer materials is an important process affecting transformation rates, toxicity, and the ultimate disposition of organic chemicals in the environment. Extensive research, focusing on the partitioning of neutral organic compounds, has shown that adsorption of these compounds generally is controlled by hydrophobic interactions. As a result, the affinity that a natural sorbent has for neutral organic solutes, in most cases, can be reliably estimated from characterization (quantification) of the hydrophobicity of chemical and sorbent. Organic carbon content has been used almost exclusively as a measure of the hydrophobic nature of natural sedimentary material. (Organic matter or volatile solids content has also been used but not as widely.) To quantitatively characterize the hydrophobicity nature of organic compounds, researchers have used various measurable parameters, including octanol-water partition constants, water solubility (corrected for crystal energy), reverse phase HPLC retention, and topological parameters of the compounds such as calculated surface area. Generally, octanol-water partition coefficients have been used more extensively, not only for estimating the partitioning of organic compounds to sedimentary materials, but also for estimating bioaccumulation of organic compounds to aquatic organisms.

The estimated and measured octanol-water partition coefficients ($K_{ow}$'s) of the neutral compounds of concern are listed in Table 6. The GEMS (Graphical Exposure Modeling System) values are estimates. All literature $K_{ow}$ values provided in Table 6 are stated as being measured in the original references except for the values given in Mabey et al. (14), which are estimates.

The partition coefficients, normalized for organic carbon content, have been calculated using the relationship,

$$\log K_{oc} = \log K_{ow} - 0.32 \qquad (5)$$

given by Hassett et al. (34). This correlation was calculated from adsorption isotherms of 13 organic chemicals, representing several classes of compounds, using 14 different sediment and soil samples. As can be seen by comparing log $K_{oc}$ values calculated using this equation to various measured log $K_{oc}$ values reported in Table 6, this correlation adequately predicts partitioning of several classes of organic compounds, including chlorinated and nonchlorinated aromatic and alkyl hydrocarbons. Use of this correlation will generally be valid for soils, sediments, and aquifer materials that have organic carbon contents greater that 0.1%.

## TABLE 6. Log $K_{ow}$ and Log $K_{oc}$ Values of Neutral Organic Toxicity Characterisic Contaminants[a]

| CHEMICAL NAME | CAS NO. | Log $K_{ow}$ GEMS[b] | Log $K_{ow}$ literature[c] | Log $K_{oc}$ calculated[d] | Log $K_{oc}$ literature[e] |
|---|---|---|---|---|---|
| ACRYLONITRILE | 107-13-1 | 0.25 | 0.25 (14)<br>1.20 (28) | -0.089 | |
| BENZENE | 71-43-2 | 2.14 | 2.11 (20)<br>2.13 (15)<br>2.12 (23) | 1.80 | 1.78 |
| BIS(2-CHLOROETHYL) ETHER | 111-44-4 | 1.00 | 1.46 (14)<br>1.12 (28) | 0.80 | |
| CARBON DISULFIDE | 75-15-0 | | 2.16 (37) | 1.84 | |
| CARBON TETRACHLORIDE | 56-23-5 | 2.88 | 2.73 (23) | 2.41 | |
| CHLORDANE, TECHNICAL (CIS) | 57-74-9 | | 6.25 (36) | 5.93 | |
| CHLOROBENZENE | 108-90-7 | 2.86 | 2.71 (22)<br>2.84 (17) | 2.39 | |
| CHLOROFORM | 67-66-3 | 1.95 | 1.90 (23)<br>1.97 (19) | 1.58 | |
| 1,4-DICHLOROBENZENE | 106-46-7 | 3.57 | 3.37 (23) | 3.05 | |
| 1,2-DICHLOROBENZENE | 95-50-1 | 3.57 | 3.40 (23) | 3.08 | 2.54 |
| 1,2-DICHLOROETHANE | 107-06-2 | 1.46 | 1.45 (23) | 1.13 | 1.51 |
| 1,1-DICHLOROETHYLENE (VINYLIDENE CHLORIDE) | 75-35-4 | 2.11 | 1.83 (14) | 1.79 | |
| 2,4-DINITROTOLUENE | 121-14-2 | 2.00 | 1.98 (14) | 1.68 | |
| ENDRIN | 72-20-8 | | 4.92 (36) | 4.60 | |
| HEPTACHLOR | 76-44-8 | | 5.53 (36) | 5.21 | |
| HEXACHLORO-1,3-BUTADIENE | 87-68-3 | 4.30 | 4.78 (23) | 4.46 | |
| HEXACHLOROBENZENE | 118-74-1 | 6.42 | 5.5 (18)<br>6.41 (14) | 5.18 | |
| HEXACHLOROETHANE | 67-72-1 | 4.61 | 3.93 (28)<br>4.62 (14) | 3.61 | |
| ISOBUTANOL (ISOBUTYL ALCOHOL) | 78-83-1 | 0.69 | 0.76 (34) | 0.44 | |
| LINDANE (HEXACHLOROCYCLOHEXANE) | 58-89-9 | 3.75 | 3.72 (27) | 3.40 | 3.30 |
| METHOXYCHLOR | 72-43-5 | | 5.08 (20) | 4.76 | 4.90 |
| METHYL ETHYL KETONE | 78-93-3 | 0.26 | 0.29 (19) | -0.03 | |
| METHYLENE CHLORIDE | 75-09-2 | 1.25 | 1.25 (16) | 0.93 | |
| NITROBENZENE | 98-95-3 | 2.03 | 1.83 (23)<br>1.85 (17)<br>1.79 (30) | 1.51 | |
| 1,1,1,2-TETRACHLOROETHANE | 630-20-6 | 3.03 | None | 2.71 | |
| 1,1,2,2-TETRACHLOROETHANE | 79-34-5 | 2.64 | 2.39 (23)<br>2.66 (14) | 2.07 | 1.90 |
| TETRACHLOROETHYLENE (PERCHLOROETHYLENE) | 127-18-4 | 3.02 | 2.53 (23)<br>2.45 (14) | 2.21 | 2.56 |
| TOLUENE | 108-88-3 | 2.79 | 2.21 (23)<br>2.69 (17) | 1.89 | |
| TOXAPHENE | 8001-35-2 | | 4.63 (36) | 4.31 | |
| 1,1,1-TRICHLOROETHANE | 71-55-6 | 2.48 | 2.47 (23)<br>2.51 (14) | 2.15 | 2.25 |
| 1,1,2-TRICHLOROETHANE | 79-00-5 | 2.05 | 2.07 (14) | 1.73 | |
| TRICHLOROETHYLENE | 79-01-6 | 2.27 | 2.42 (23) | 2.10 | |
| VINYL CHLORIDE | 75-01-4 | 1.36 | 1.23 (14) | 1.04 | |

FOOTNOTES:

a. Recommended values are underlined.
b. Estimated value. GEMS (Graphical Exposure Modeling System) is a computer system under management of the Office of Toxic Substances, Exposure Evaluation Division, installed on the OTS VAX 11/780 computer in Research Triangle Park, NC.
c. Measured values, except those reported by reference (14).
d. Calculated using log $K_{oc}$ = log $K_{ow}$ -0.32 (34).
e. Karickhoff, 1981; and references therein.

## 2.2 Ionizable Compounds

Predicting the partitioning of ionizable organic compounds is not as straightforward as for the neutral compounds. These compounds, whether they are acids or bases, can exist as ions in solution depending upon the pH of the solution according to the following equations. For acids,

$$K_a = (H^+)(A^-)/(HA) \quad (6)$$

and bases,

$$K_a = (H^+)(B)/(HB^+) \quad (7)$$

where $(H^+)$ is the hydrogen ion activity, $(HA)$ is the neutral organic acid activity (or concentration), $(A^-)$ is the organic acid anion activity, $(B)$ is the neutral organic base activity, $(HB^+)$ is the protonated organic base activity, and $K_a$ is the acid dissociation constant. Among the toxicity characteristic compounds are ten organic acids that have $pK_a$ ($-\log K_a$) values of relevance to environmental systems ($4 < pH < 10$). One compound (pyridine) is an organic base.

In general, more effort has been expended investigating the sorption of organic acids than the sorption of organic bases. For the organic acids, adsorption can be modeled to sediments, soils, and aquifer materials in a similar manner to that of the neutral compounds, after taking into account ionization, as long as the pH is not more than one unit above the $pK_a$ of the compound (see Schellenberg et al., 1984). For the compounds of interest, this means that the $K_{oc}$ can be calculated directly from the $K_{ow}$ for the compounds m-cresol, o-cresol, p-cresol, and phenol, as these compounds are essentially all in their neutral form at pH 7.0 ($pK_a - pH > 2$). The regression equation (Schellenberg, et al 1984) for these compounds

$$K_{oc} = 1.05\ K_{ow}^{(0.82)} \quad (8)$$

has been used to calculate the $K_{oc}$ values given in Table 7.

For 2,4,5-trichlorophenol and 2,4,6-trichlorophenol $[0 < (pH - pK_a) < 1]$, the same relationship can be used to calculate a $K_{oc}$ at pH 7 if acid dissociation is accounted for, using Equation 9.

$$K_{oc} = 1.05\ K_{ow}^{(0.82)}(1.0/(1.0 + K_a/(H^+))) \quad (9)$$

These and other chlorinated phenols were used by Schellenberg et al. (25) to develop this relationship.

The remaining compounds (2,4-D, silvex, 2,3,4,6-tetrachlorophenol, and pentachlorophenol) are more problematic. Because of their low $pK_a$ values, adsorption of these compounds occurs predominantly by the anionic species (Jafvert, 1990). Therefore, an estimate of a partition coefficient from the $K_{ow}$ of the neutral species would significantly overestimate the magnitude of adsorption. Jafvert et al. (26) and Jafvert (35) have investigated the partitioning behavior of these and similar compounds in the octanol-water

system and in sediment- and soil-water systems. For example, Jafvert (35) has reported on the sediment-water distribution of silvex in 13 soils or sediments. If the partition coefficients (in which the pH of the slurry is greater than 7) are regressed versus the fraction organic carbon, a value of log $K_{oc}$ = 1.8 is obtained. The log $K_{ow}$ of the neutral form of silvex is 3.8. Similar results for pentachlorophenol and 4-chloro-a-(4-chlorophenyl)-benzeneacetic acid (DDA) suggest that the partition coefficient (at pH 7.0) of the anionic form of these compounds is approximately two orders of magnitude less than the respective $K_{ow}$'s of the neutral form of these compounds. The log $K_{oc}$ values reported in Table 7 are estimated for pH 7, and reflect this difference.

Unlike anionic organic compounds, which partition more weakly than their neutral counterparts, organic cations tend to partition more strongly than the corresponding unprotonated bases. Also, unlike the organic anions, which partition largely through modified (by the negative charge) hydrophobic interactions, the organic cations can undergo cation (or ligand) exchange reactions. Pyridine, one of the compounds of concern, is an organic base that has a $pK_a$ value of 5.36. At pH 7, a small fraction (2.2%) of pyridine will exist as an organic cation in aqueous solution. Because the cationic species is expected to adsorb more strongly to most natural soils, sediments, and aquifer materials than the neutral species, an organic-carbon-normalized partition coefficient may severely under-estimate the adsorption of this compound at near-neutral pH. Because no predictive methods exist for describing the partitioning of organic cations to natural matrices, however, the organic-carbon-normalized partition coefficient (calculated from the $K_{ow}$ of the neutral species, and not accounting for ionization) is given in Table 7. For virtually every sediment and aquifer material, this constant will under-predict the true magnitude of adsorption of this compound, with the error intensifying as the organic carbon content of a sediment or aquifer material decreases.

TABLE 7. Log $K_{ow}$, Log $K_{oc}$, and $pK_a$ Values for Ionizable Organic Compounds[a]

| CHEMICAL NAME | CAS NO. | Log $K_{ow}$ GEMS | Log $K_{ow}$ literature | Log $K_{oc}$ calculated at pH 7 | $pK_a$ literature |
|---|---|---|---|---|---|
| | | | * * * ORGANIC ACIDS * * * | | |
| 2,4-D | 94-75-7 | 2.52 | <u>2.83</u> (26)<br>2.81 (17) | 0.83[b] | <u>2.90</u> (26) |
| M-CRESOL | 108-39-4 | 2.12 | <u>1.95</u> (31) | 1.62[c] | <u>10.0</u> (24) |
| O-CRESOL | 95-48-7 | 2.12 | <u>2.04</u> | 1.69[c] | <u>10.2</u> (24) |
| P-CRESOL | 106-44-5 | 2.12 | <u>1.95</u> (31) | 1.62[c] | <u>10.2</u> (24) |
| PENTACHLOROPHENOL | 87-86-5 | 5.06 | <u>5.09</u> (26)<br>5.24 (25) | 3.09[b] | <u>4.83</u> (26)<br>4.75 (25) |
| PHENOL | 108-95-2 | 1.48 | <u>1.46</u> (17) | 1.22[c] | <u>9.96</u> (24) |
| SILVEX (2,4,5-TP) | 93-72-1 | | <u>3.80</u> (26) | 1.80[b] | <u>3.07</u> (26) |
| 2,3,4,6-TETRACHLOROPHENOL | 58-90-2 | 4.32 | <u>4.42</u> (25) | 2.42[b] | <u>5.40</u> (25) |
| 2,4,5-TRICHLOROPHENOL | 95-95-4 | 3.85 | <u>4.19</u> (25) | 3.12[d] | <u>6.94</u> (25) |
| 2,4,6-TRICHLOROPHENOL | 88-06-2 | 3.85 | <u>3.72</u> (25) | 2.12[d] | <u>6.10</u> (25) |
| | | | * * * ORGANIC BASES * * * | | |
| PYRIDINE | 110-86-1 | 0.66 | <u>0.65</u> (33) | 0.33[e] | <u>5.36</u> (24) |

FOOTNOTES:

a. Recommended values are underlined.
b. Jafvert, assumes partitioning of ion to be a factor of 2 less than neutral species (35).
c. Calculated from $K_{oc} = 1.05\ K_{ow}^{(0.82)}$
d. Calculated from $K_{oc} = 1.05\ K_{ow}^{(0.82)}\ (1.0/(1.0+K_a/[H^+]))$, where $[H^+] = 1.0 \times 10^{-7}$ M (25).
e. Calculated from $\log K_{oc} = \log K_{ow} - 0.32$ (34).

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